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(54) ALUMINUM-PLATED STAINLESS STEEL SHEET WITH EXCELLENT HIGH-TEMPERATURE OXIDATION RESISTANCE

(57) An aluminum-plated stainless steel sheet with an excellent high-temperature oxidation resistance, produced by plating with aluminum or an aluminum-base alloy a ferritic stainless steel sheet comprising on the weight basis at most 0.05 % of carbon, at most 1.0 % of silicon, at most 1.0 % of manganese, 10-30 % of chromium, at most 0.05 % of nitrogen, 0.1-4.0 % of molybdenum, and 0.01-2.2 % in total of one or more elements selected from the group consisting of rare earth elements and yttrium, further containing, as the case may be, (% C + % N)X4-0.8 % in total of one or more elements selected from the group consisting of titanium, niobium, vanadium and zirconium, further containing, if necessary, at most 6.0 % of aluminum, and the balance consisting of iron and inevitable impurities.

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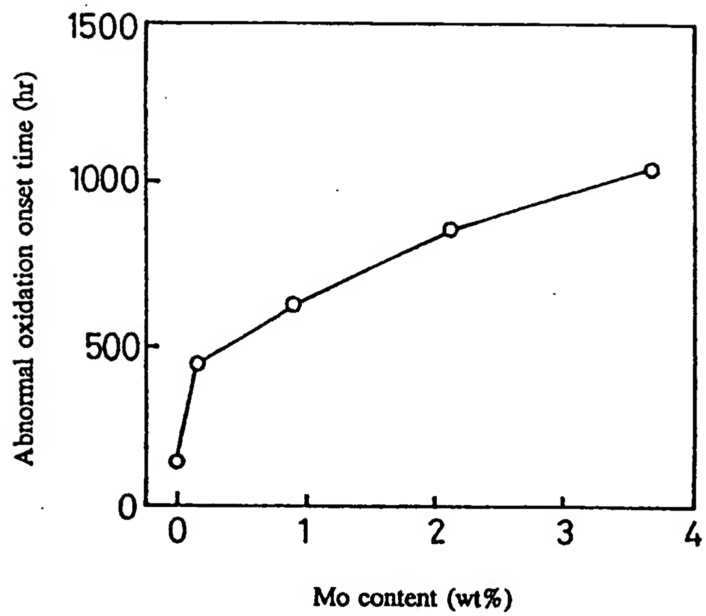
Figure 1


1500
1000
500
0
0
1
2
3
4
Abnormal oxidation onset time (hr)
Mo content (wt%)

Field of the Invention

The present invention relates to an Al-coated stainless steel sheet that has very good high-temperature oxidation resistance.

Background of the Field

Al-coated stainless steel, formed by coating stainless steel with aluminum or an aluminum-based alloy, exhibits good resistance to heat and corrosion, and therefore is used extensively in applications in which resistance to heat and/or corrosion is required. Typical heat-resistance applications include combustion equipment, heating equipment, and automotive exhaust system tubing and exhaust cleaning devices (catalytic support).

It is known that good high-temperature oxidation resistance is exhibited by Al-coated ferritic stainless steel sheet containing, by weight, up to 6% Al, up to 1.0% rare earth metals (REM), Y, and Ti and Nb or the like added in an amount sufficient to fix C + N. There has been disclosed the use of such a material as, in particular, a support material for the catalyst used in automotive exhaust gas cleaning devices. For example, in the field of catalytic support materials for use in automotive exhaust gas cleaning devices in which a layer of aluminum coated on ferritic stainless steel foil is heat treated to form an aluminum oxide coating to support a catalyst, JP-A-61-281861 discloses adding Al to the base steel of the foil, JP-A-62-11547 discloses the addition of Al and Ti, JP-A-HEI-5-140766 discloses the addition of rare earth metals and/or Y, and JP-A-HEI-1-159384 discloses the addition of Al and rare earth metals and/or Y.

Also with respect to catalytic support material, in JP-A-64-15144 and JP-A-HEI-2-26643 the present inventors disclosed that by adding Al, one or more selected from Ti, Nb, V, and Zr, and rare earth metals, to the base ferritic stainless steel, the oxidizing treatment of the Al-coated product results in the formation of a stable layer of aluminum oxide. The present inventors also taught that the high-temperature strength of the material could be improved by adding up to 2.0% Mo to the base steel.

In JP-A-HEI-5-112859, it was shown that the corrosion-resistance of automotive exhaust system mufflers of Al-coated stainless steel in an exhaust gas condensation (condensate) environment could be improved by adding an appropriate amount of Mo to the base ferritic stainless steel sheet material.

Object of the Invention

As described in the above disclosures, conventional Al-coated stainless steel sheet developed for heat-resisting applications does indeed have good heat resistance. However, there has been rising demand for Al-coated stainless steel sheet that can be used under severe high-temperature conditions that are beyond the capabilities of the conventional materials. The ability to not undergo abnormal oxidation even after extended exposure to an oxidizing atmosphere at elevated temperatures as high as 1150°C or 1250°C, for example, is required of turbine peripheral materials, boiler materials, catalytic metal support materials used in exhaust gas cleaning devices for high-temperature engines, and in other such applications. Here, abnormal oxidization refers to local peeling and splitting of a heat-resistant, protective layer of Al or Cr oxides or the like formed on an Al-coated stainless steel sheet surface, leading to the rapid advance of oxidation, the abnormal spread of ferric oxides and the sudden loss of heat resistance.

When this happens, especially in the case of thin material not thicker than 100 µm, such as for example Al-coated stainless steel foil 50 µm thick, even if aluminum from the Al coating diffuses into the base steel, enriching the Al content of the steel, since there is limit to the absolute amount, the Al in the steel is exhausted by a short period of heating, forming Al oxide, giving rise to abnormal oxidation under high-temperature conditions.

The object of the present invention is therefore to provide Al-coated stainless steel sheet having better high-temperature oxidation resistance that does not exhibit abnormal oxidation in a high-temperature oxidising atmosphere that is more severe than that which can be withstood by conventional heat-resistant Al-coated stainless steel sheet.

Disclosure of the Invention

In accordance with this invention, there is provided an Al-coated stainless steel sheet having good high-temperature oxidation resistance formed by coating a ferritic stainless steel sheet with aluminum or aluminum-based alloy, said steel comprising, by weight:

up to 0.05% C,

up to 1.0% Si,
up to 1.0% Mn,
from 10.0% to 30.0% Cr,
up to 0.05% N,
from 0.1% to 4.0% Mo,
a total of from 0.01% to 0.2% of one or more elements selected from a group comprised of rare earth metals and Y,
a total of (%C + %N) x 4.0% to 0.8% of one or more elements selected from a group comprised of Ti, Nb, V, and Zr,
and optionally containing up to 6.0% Al,
the balance being iron and unavoidable impurities.

Brief Description of the Drawing

Figure 1 is a graph illustrating the relationship between Mo content and time taken for abnormal oxidation to arise in Al-coated stainless steel in a first example of the invention.

Detailed Description of the Invention

The Al-coated stainless steel sheet according to the present invention exhibits high-temperature oxidation resistance at higher temperatures than those achievable with conventional heat-resistant Al-coated stainless steel sheet. Moreover, as shown hereinbelow in the examples, even Al-coated stainless steel sheet that is very thin, such as for example stainless steel foil only 50 μm thick, does not exhibit abnormal oxidation even after being left for an extended period of time in an oxidising atmosphere at a temperature of from 1150°C to 1250°C. Such properties cannot be obtained with Al-coated stainless steel sheets of the prior art.

The excellent high-temperature oxidation resistance of the Al-coated stainless steel sheet of this invention results from using ferritic stainless steel sheet having the above composition as the base steel sheet. In particular, including appropriate amounts of rare earth metals or Y, or both, and Mo is useful for imparting high-temperature oxidation resistance.

It is known that Mo improves the high-temperature strength of ferritic stainless steel and is also effective for improving the corrosion resistance of ferritic stainless steel. However, when the steel is placed in a high-temperature oxidizing atmosphere the Mo in the steel does not form surface oxides that are stable at high temperatures. Thus, not only has Mo been considered an element that does not contribute to improving high-temperature oxidation resistance, but has been considered an element that actually degrades the high-temperature oxidation resistance of the steel.

However, the present inventors found that the high-temperature oxidation resistance of Al-coated stainless steel sheet could be markedly improved, as shown in Table 1 and Figure 1, when the base ferritic stainless steel contains an appropriate amount of Mo. Why this is so is not completely clear. However, it is assumed that, compared to when Mo is not added, Al-coated stainless steel sheet with added Mo produces a denser coating of aluminum oxide with a very low growth rate. This means the reduction of Al diffused in the steel is slowed, so for an extended period of time the Al does not become exhausted. In addition, as the amount of Al in the steel decreases, a layer of chromium oxide starts to form below the aluminum oxide layer, and even after the aluminum is exhausted, a degree of high-temperature oxidation resistance is maintained by this chromium oxide layer. Thus, it is surmised that a suitable amount of Mo in the steel functions to promote the formation of a dense aluminum oxide layer that has good adhesion to the base steel, markedly suppress the decrease of Al in the steel and promote the formation of a chromium oxide film when the Al in the steel has decreased, and that, taken together, the overall effect is to contribute to markedly raise the high-temperature oxidation resistance of the Al-coated stainless steel sheet concerned.

While the degree of this contribution might differ depending on whether the coating is aluminum or aluminum based alloy, the effect itself is substantially the same. Aluminum based alloy as used herein refers to the aluminum based alloy coating that is commonly applied to ferritic stainless steel, and more specifically, to aluminum based alloy coating in which the aluminum contains up to 11% by weight silicon. In some cases, the aluminum may contain Mn, Mg, Cr or the like as alloying elements. As used herein, Al-coated is a general term encompassing aluminum coating and aluminum based alloy coating.

The reasons for the limitations on the chemical components of the base steel of the Al-coated stainless steel sheet according to this invention, will now be described in specific detail together with the function thereof.

For increasing the high-temperature oxidation resistance of Al-coated stainless steel sheet, a low C content in the base steel sheet is preferable. Carbon in the steel has the effect of obstructing the diffusion of aluminum from the aluminum coating into the base steel, when the Al-coated stainless steel sheet is heated. Thus, a base steel C content of up to 0.05% by weight, and preferably up to 0.03%, is specified. However, since the amount of solid solution C having the above effect is decreased by the addition of elements such as Ti, Nb, V, and Zr that form compounds with C and N in the steel, no upper limit is specified for the C content.

Si hardens the steel and reduces the toughness, so a Si content not exceeding 1.0% by weight is preferable.

Too high a Mn content degrades the high-temperature oxidation resistance of Al-coated stainless steel sheet, so a Mn content not exceeding 1.0% by weight is preferable.

Cr is a basic component for obtaining Al-coated steel sheet that has high-temperature oxidation resistance, for which at least 10% Cr is required. However, a Cr content that exceeds 30% does not result in any marked improvement in the effect, and too much Cr can degrade the workability. Therefore, a base steel Cr content of from 10% to 30% by weight is specified.

N combines with Al diffused into the base steel from the aluminum coating layer to form AlN, which hinders the diffusion of Al. A low N content is therefore preferable, and so a N content of up to 0.05% by weight is specified. However, as is the case with carbon, since the amount of solid solution N having the above effect is decreased by the addition of elements such as Ti, in such cases no upper limit is specified for the N content.

Mo plays a very important role in increasing the high-temperature oxidation resistance of Al-coated stainless steel sheet. As described in the following examples, this effect is manifested when the Mo content is at least 0.1%. However, an amount of Mo that exceeds 4% degrades the toughness of stainless steel and makes it more difficult to produce. The Mo content in the base stainless steel is therefore set at from 0.1% to 4.0% by weight, and more preferably at from 0.5% to 4.0% by weight.

Rare earth metals and Y have the effect of improving the adhesion of the aluminum oxide film formed on the surface of Al-coated steel sheet. This effect is manifested when a total of at least 0.01% by weight of one or more elements selected from the rare earth metals and Y is added. However, a total added amount that exceeds 0.2% gives rise to the precipitation of inclusions in the base steel, degrading the high-temperature oxidation resistance. Therefore, the total content of one or more elements selected from a group comprised of rare earth metals and Y has been set at from 0.01 to 0.2 wt%.

Ti, Nb, V, and Zr each form compounds with C and N in the steel, thereby fixing the carbon and nitrogen. This prevents the carbon and nitrogen in the steel from hindering the diffusion into the steel of aluminum from the aluminum coating and also improves the toughness of stainless steel. Thus, it is preferable for these elements to be present in a sufficient amount to combine with the carbon and nitrogen in the steel, specifically, in an amount that is at least (%C + %N) x 4. Since too high a content degrades the workability of stainless steel, a total upper limit of 0.8 wt% has been specified for these elements.

In this invention, the aluminum in the aluminum coating forms the principal source of the aluminum for the aluminum oxide film. For this purpose, the amount of aluminum normally used as a deoxidizing agent during the steelmaking process is sufficient. Adding aluminum to the base stainless steel can further enhance the high-temperature oxidation resistance. However, an Al content that exceeds 6% can degrade the toughness of the slab and hot-rolled strip, making it difficult to produce the steel. Thus, if required, the base stainless steel can be given up to 6.0 wt% Al.

The Al-coated stainless steel sheet according to this invention comprises aluminum coated or aluminum alloy coated ferritic stainless steel sheet having the above components and composition. Compared to conventional Al-coated stainless steel sheet material, the Al-coated stainless steel sheet of this invention can withstand severer high-temperature oxidation conditions without exhibiting abnormal oxidation. Any method can be used to effect the aluminum or aluminum alloy coating that ensures good adhesion with the base stainless steel. Evaporation and electroplating are examples of suitable coating methods. In some cases, cladding or spraying may be used.

Examples

Example 1

Stainless steel foils 50 µm thick having the compositions shown in Table 1 were prepared. Both sides of the foils were then given a 3-µm-thick coating of aluminum by evaporation, the foils were subjected to oxidation tests by being maintained at 1150° C under atmospheric conditions, and the effect of Mo content

on the abnormal oxidation onset time was investigated. Table 1 also lists the results. The abnormal oxidation onset time is shown as total heating time, from when a test specimen is removed from the furnace and the surface visually inspected to the point at which brown, ridged oxides are observed in addition to the normal thin, protective, uniform oxide layer. Figure 1 is a graph of the relationship between abnormal oxidation onset time and steel Mo content.

TABLE 1

	Specimen	Components and contents of coated base material (wt%)									Abnormal oxidation onset time (hours)
		C	Si	Mn	P	S	Cr	Mo	N	REM	
Comparative	No. 1	0.015	0.30	0.23	0.020	0.0021	20.0	0	0.013	0.09	140 h
Inventive	No. 2	0.018	0.27	0.25	0.023	0.0023	20.1	0.15	0.012	0.09	450 h
	No. 3	0.016	0.28	0.22	0.021	0.0022	20.1	0.87	0.011	0.10	620 h
	No. 4	0.016	0.32	0.23	0.022	0.0025	20.2	2.11	0.012	0.09	850 h
	No. 5	0.017	0.26	0.27	0.025	0.0020	20.0	3.67	0.014	0.10	1,040 h

Table 1 and Figure 1 reveal that the abnormal oxidation onset time gets longer as the Mo content is increased, and that this effect starts to occur when the Mo content is in the order of 0.1%. This is considered to be caused by the added Mo suppressing the growth of the aluminum oxide film. In particular, the marked improvement in oxidation resistance at such a high temperature, even when the base stainless steel is foil only 50 µm thick, shows that the aluminum diffused in the steel foil does not become exhausted for an extended period of time. Expressed another way, it can be considered that the growth of the aluminum oxide film is effectively suppressed owing to the existence of Mo. Whatever the reason, in the case of the steel of the comparative specimen (No. 1), which contained the same amounts of the other components but no Mo, abnormal oxidation occurred in a relatively short 140 hours, while in the case of the inventive steels (Nos. 2 to 5) containing from 0.1 to 4.0 wt% Mo the high-temperature oxidation resistance was markedly improved, abnormal oxidation taking a very long time to occur.

Example 2

0.3-mm-thick stainless steel sheet having the composition shown in Table 2 was given an approximately 150 g/m^2 coating of Al - 9.5% Si alloy by the aluminum hot dip method, and then rolled to form Al-coated stainless steel foil 50 µm thick. As in Example 1, the foils were then subjected to oxidation tests by being maintained at 1150°C under atmospheric conditions. Table 1 also lists the time it took for each of the tested Al-coated stainless steel foils to exhibit abnormal oxidation.

TABLE 2

	Specimen	Components and contents of coated base material (wt%)																Abnormal oxidation onset time (hours)
		C	Si	Mn	P	S	Cr	Mo	N	La	Ce	Y	Al	Ti	Nb	Zr	V	
Inventive	No. 6	0.012	0.03	0.22	0.018	0.0019	11.2	2.11	0.010	0.05	0.04	-	-	-	-	-	-	510 h
	No. 7	0.037	0.42	0.38	0.032	0.0113	13.1	1.97	0.012	0.11	-	0.06	0.12	-	0.07	0.10	-	620 h
	No. 8	0.011	0.25	0.26	0.021	0.0042	17.2	2.04	0.009	-	-	0.12	-	-	-	-	-	940 h
	No. 9	0.010	0.07	0.09	0.024	0.0028	19.4	2.10	0.012	0.07	-	-	0.06	0.17	-	-	-	1,070 h
	No. 10	0.027	0.32	0.24	0.026	0.0026	24.5	2.08	0.017	0.02	0.06	0.03	0.27	-	-	-	-	1,160 h
	No. 11	0.014	0.11	0.23	0.025	0.0021	25.3	1.95	0.013	-	-	0.10	-	0.07	0.06	-	-	1,200 h
	No. 12	0.009	0.44	0.48	0.040	0.0081	28.2	1.93	0.028	-	0.01	-	-	-	-	-	0.09	1,240 h
Comparative	No. 13	0.011	0.28	0.29	0.026	0.0070	7.6	2.06	0.012	-	-	0.10	-	-	-	-	-	330 h
	No. 14	0.020	0.19	0.27	0.019	0.0023	19.7	2.10	0.017	-	-	-	0.08	0.12	-	-	-	140 h
	No. 15	0.157	0.33	0.20	0.032	0.0054	20.2	1.98	0.088	0.06	0.04	-	-	-	-	-	-	90 h

Table 2 shows that in each of the inventive specimens (Nos. 6 to 12) in which the amount of each component in the base steel is within the range according to this invention, abnormal oxidation onset time is over 500 hours, indicating a marked improvement in the high-temperature oxidation resistance. In contrast, in comparative specimen No. 13 in which the Cr content is less than 10 wt%, comparative specimen No. 14 in which the total content of rare earth metals and Y is less than 0.01 wt% and comparative specimen No.

15 in which the C content and N content are each over 0.05 wt%, the abnormal oxidation onset time is a short 400 hours or less.

Example 3

Each side of stainless steel foils 50 µm thick having the compositions shown in Table 1 was given a 2-µm-thick coating of aluminum by evaporation, the foils were subjected to oxidation tests at 1150° C, as in Example 1, and the effect of the absence or presence of aluminum coating on abnormal oxidation onset time was investigated. The results are listed in Table 3.

TABLE 3

	Specimen	Components and contents of coated base material (wt%)											Al-coated	Abnormal oxidation onset time (hours)
		C	Si	Mn	P	S	Cr	Mo	N	REM	Al	Ti		
Invention	No. 16	0.015	0.10	0.27	0.031	0.0010	19.6	2.16	0.013	0.09	3.2	0.14	Yes	1,090 h
Comparative													No	350 h
Invention	No. 17	0.013	0.09	0.22	0.026	0.0042	20.1	0.83	0.011	0.06	5.1	—	Yes	1,020 h
Comparative													No	380 h

Table 3 shows that each of the Al-coated steel foils according to the invention exhibited an abnormal oxidation onset time of over 1000 hours, indicating a marked improvement in the high-temperature oxidation resistance of the material. In contrast, the abnormal oxidation onset time in the case of steel foil that had not been Al-coated was a relatively short 400 hours or less.

Example 4

Ferritic stainless steel sheets No. 5 and No. 1 (each 0.25 mm thick) listed in Table 1 were given a 200 g/m^2 coating of Al - 9% Si alloy by the aluminum hot dip method, and then rolled to form Al-coated stainless steel foil 50 μm thick. The foils were then subjected to the same oxidation tests as Example 1 at a temperature of from 1150°C to 1250°C and the abnormal oxidation onset times investigated. The results are listed in Table 4.

Table 4

Steel No.	Abnormal oxidation onset time at each temperature			Remarks
	1150°C	1200°C	1250°C	
5	2360 hr	1070 hr	350 hr	Invention
1	250 hr	80 hr	20 hr	Comparative

The base steels Nos. 5 and 1 of the Al-coated stainless steel foils have the same composition contents, except for Mo, which is contained in steel No. 5 but not in steel No. 1. As shown by Table 4, at each temperature the Mo-containing steel No. 5 exhibits a far longer abnormal oxidation onset time than steel No. 1 which does not contain Mo. At 1250° C steel No. 5 exhibited an abnormal oxidation onset time of 350 hours, providing a high-temperature oxidation resistance not attainable with the conventional steel material.

Thus, in accordance with the present invention, Al-coated stainless steel sheet is provided that can withstand use under high-temperature conditions that are beyond the ability of conventional Al-coated stainless steel sheet to withstand. As such, the present invention can expand the range of application of such steel materials to turbine peripheral materials, boiler materials, catalytic metal support materials used in exhaust gas cleaning devices for high-temperature engines, and other such fields.

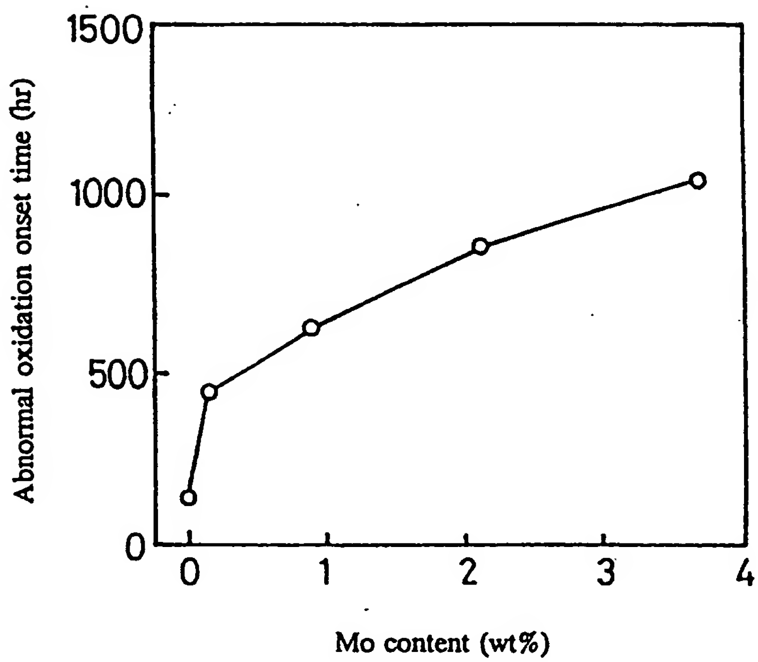
Claims

1. Al-coated stainless steel sheet having good high-temperature oxidation resistance formed by coating a ferritic stainless steel sheet with aluminum or aluminum-based alloy, said steel comprising, by weight:
up to 0.05% C,
up to 1.0% Si,
up to 1.0% Mn,
from 10.0% to 30.0% Cr,
up to 0.05% N,
from 0.1% to 4.0% Mo,
a total of from 0.01% to 0.2% of one or more elements selected from a group comprised of rare earth metals and Y,
the balance being iron and unavoidable impurities.

2. Al-coated stainless steel sheet having good high-temperature oxidation resistance formed by coating a ferritic stainless steel sheet with aluminum or aluminum-based alloy, said steel comprising, by weight:
up to 0.05% C,
up to 1.0% Si,
up to 1.0% Mn,
from 10.0% to 30.0% Cr,
up to 0.05% N,
from 0.1% to 4.0% Mo,
a total of from 0.01% to 0.2% of one or more elements selected from a group comprised of rare earth metals and Y,
a total of (%C + %N) x 4.0% to 0.8% of one or more elements selected from a group comprised of Ti, Nb, V, and Zr,
the balance being iron and unavoidable impurities.

3. The Al-coated stainless steel sheet according to claim 1 or 2, in which the ferritic stainless steel sheet contains up to 6.0 wt% Al.

Figure 1


1500
1000
500
0
Abnormal oxidation onset time (hr)
0
1
2
3
4
Mo content (wt%)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP94/02245

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl[6] C22C38/22, 38/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[6] C22C38/00-38/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926 - 1994
Kokai Jitsuyo Shinan Koho 1971 - 1994

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 4-354850 (Nisshin Steel Co., Ltd.), December 9, 1992 (09. 12. 92), Lines 2 to 18, column 1 (Family: none)	1-3
A	JP, A, 2-232345 (Sumitomo Metal Industries, Ltd.), September 14, 1990 (14. 09. 90), Lines 14 to 27, column 1 & US, A, 5069870	1-3
A	JP, A, 4-362127 (Nisshin Steel Co., Ltd.), December 15, 1992 (15. 12. 92), Lines 2 to 40, column 1 (Family: none)	1-3
A	JP, A, 2-179853 (Kawasaki Steel Corp.), July 12, 1990 (12. 07. 90), Lines 14 to 28, column 1, lines 10 to 14, column 2 (Family: none)	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
March 27, 1995 (27. 03. 95)	April 4, 1995 (04. 04. 95)

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